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RATE CONSTANTS FOR SOME OXIDATIONS OF S(IV) BY RADICALS IN AQUEOUS SOLUTIONS

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Abstract—Rate constants were measured for several radical reactions important in the autoxidation of S(IV) in atmospheric droplets. For the reactions of the hydroxyl radical with sulfite and bisulfite, the rate constants were found to be 5.2×10^9 and 4.5×10^9 $M^{-1}s^{-1}$, respectively. For the reaction of the dichloride radical anion with bisulfite, a rate constant of 3.4×10^8 $M^{-1}s^{-1}$ was obtained. The peroxysulfate radical was found to react with sulfite with a rate constant of 1.3×10^7 $M^{-1}s^{-1}$, but only an upper limit of 3×10^5 could be derived for its reaction with bisulfite. In some cases, the rate constants are significantly different from those used previously in atmospheric models. The use of these results in a simple model suggests that secondary radical–radical reactions may be of considerable importance in the mechanism of sulfite autoxidation in the atmosphere.

Key word index: Acid rain, free radicals, aqueous chemistry, sulfite.

INTRODUCTION

In a recent issue of this Journal, McElroy (1986) discussed the impact of the OH radical on the oxidation of SO_2 in atmospheric droplets. The reaction of this radical with dissolved SO_2 (sulfite and bisulfite) initiates a chain reaction, leading, potentially, to the oxidation of many more sulfite or bisulfite molecules. In order to assess the importance of this oxidation mode, reliable rate data are needed for key reactions in this chain. Further, other constituents of the droplet can react with the dissolved OH, or with chain-carrying radicals, and influence the rate at which S(IV) is oxidized. Specifically, McElroy found that Cl^- could have a significant impact, but that its impact depended on the rate constant for the reaction of the peroxysulfate radical with bisulfite. Since a thorough understanding of the radical chain mechanism for SO_2 oxidation in aqueous systems is important both for an improved understanding of the acidification of atmospheric droplets by the emission of SO_2 and for an improved understanding of the chemistry of lime/limestone flue-gas scrubbers, which are used to help keep SO_2 out of the atmosphere, we have measured rate constants for several of these key reactions.

EXPERIMENTAL

Rate constants were measured using a pulse radiolysis apparatus which consists of a Febetron 705 accelerator supplying 50-ns pulses of 2 MeV electrons. The dose per pulse was usually about 500 rad, determined with KSCN dosimetry. The optical detection system used a 300 W xenon lamp, separated from the cell by a shutter, and a monochromator and photomultiplier located in a separate room from the irradiation zone. Before the pulse, the optical signal was measured by a sample-and-hold circuit and the change in absorbance after the pulse monitored with a differential amplifer. The kinetic traces were digitized by a transient recorder and first-order rate constants derived with a linear least-squares routine.

Reagent-grade chemicals were used as supplied. The amount of S(IV) in the sodium bisulfite sample was determined by dissolving a sample in 6 M $HClO_4$ and measuring the absorbance at 280 nm. An SO_2 absorptivity of 367 $M^{-1}cm^{-1}$ was used (Siskos *et al.*, 1984). Water was purified by a Millipore Milli-Q system and solutions were prepared fresh each day.

The irradiation of aqueous solutions at pH 3–13 produces the hydroxyl radical and the hydrated electron in similar concentrations, along with a small ($< 10\%$) yield of hydrogen atoms. In a typical experiment, the solution is saturated with N_2O or a N_2O–O_2 mixture, and the hydrated electrons are converted rapidly to OH.

$$H_2O \rightarrow \rightarrow \rightarrow e^-_{aq}, H, OH \qquad (R1)$$

$$e^-_{aq} + N_2O \rightarrow N_2 + OH + OH^-. \qquad (R2)$$

RESULTS

(1) $OH + HSO_3^-/SO_3^{2-}$

The OH radical is probably the most important reactive radical likely to interact with an atmospheric droplet, at least in the clean troposphere. Rate constants for the reactions of OH with S(IV) have been reported only by Adams and Boag (1964), who measured the competition between that reaction and the reaction of OH with CO_3^{2-}. Rate constant ratios of 26 for $OH + HSO_3^-$ and 15 for $OH + SO_3^{2-}$ were obtained. Since neither the reactants nor products in this reaction have convenient optical absorbances, we also have resorted to competition to determine this rate constant. As the competing reactant, we have chosen para-nitrobenzoic acid (pNBA), which reacts with OH to produce a radical adduct, absorbing at 420 nm, with a rate constant near that expected for OH

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$+ HSO_3^-/SO_3^{2-}$ (Neta and Dorfman, 1968). Rate constants were derived by determining the reduction in the absorbance at 420 nm, since the product of the reaction of OH with SO_3^{2-}, the radical SO_3^-, does not absorb at this wavelength. At any concentration of added sulfite, the relative rate constant could be calculated with the equation

$$\frac{k(OH + pNBA)}{k(OH + SO_3^{2-})} = \frac{[SO_3^{2-}]}{[pNBA]} \times \frac{Abs}{Abs^o - Abs}$$

where Abs^o is the optical absorbance with no added sulfite, and Abs is the absorbance at a given sulfite concentration. All of the absorbance measurements had to be corrected for the small (6.2% of Abs^o) contribution due to the absorbance by the product of the reaction of the H atom with pNBA.

At pH 11.2, the pulse radiolysis of an N_2O saturated solution containing 1.05 mM *p*-nitrobenzoic acid resulted in an absorbance at 420 nm of 0.025 (corrected for the H atom reaction product). Upon the addition of 0.29 mM Na_2SO_3, the absorbance was reduced to 0.016, and a relative rate constant, $k(pNBA)/k(SO_3^{2-})$, of 0.49 was calculated. At 0.614 mM Na_2SO_3 the absorbance was reduced to 0.012, and a relative rate constant of 0.51 was calculated. Using a rate constant of 2.6×10^9 for OH + pNBA (Neta and Dorfman, 1968), we derive $5.2 \times 10^9 M^{-1}s^{-1}$ for $OH + SO_3^{2-}$, in very good agreement with the value derived from competition with carbonate.

Similar experiments were carried out at pH 4.4. Here, a 1.09 mM solution of pNBA gave, upon pulse radiolysis, an absorption of 0.031, which was reduced to 0.021 at 0.27 mM $NaHSO_3$, to 0.015 by 0.7 mM $NaHSO_3$, and to 0.012 by 1.05 mM $NaHSO_3$. These result in relative rate constants of 0.53, 0.58 and 0.62, respectively, with an average of 0.58. This yields an absolute rate constant of $4.5 \times 10^9 M^{-1}s^{-1}$ for OH $+ HSO_3^-$. There does seem to be a small trend in the relative rate constant, suggesting that the scavenging of OH might not be complete at the lower substrate concentrations, and becomes slightly more efficient as the bisulfite concentration is raised. Due to this possibility, and to the indirect nature of these measurements, we estimate an uncertainty of 20% in these rate constants.

The rate constant reported here for the reaction of OH with bisulfite is lower than the rate constant for the reaction of OH with sulfite. This is in line with the results for other electron transfer reactions involving sulfite and bisulfite (Neta and Huie, 1985b). The discrepancy between the present results and those derived by competition with carbonate are possibly due to the influence of bicarbonate at the lower pH.

(2) $Cl_2^- + HSO_3^-$

A significant trace species in atmospheric droplets is the chloride ion (Lazrus *et al.*, 1983). Strong oxidants such as OH, NO_3 or SO_4^- can oxidize chloride (Neta and Huie, 1986), producing a chlorine atom which equilibrates to form the dichloride radical, Cl_2^-

$$Ox + Cl^- \rightarrow Red + Cl \qquad (R3)$$

$$Cl + Cl^- \leftrightarrow Cl_2^-. \qquad (R4)$$

The impact of this reaction on the radical-initiated autoxidation of SO_2 will depend very much upon the rate constant for the reaction of Cl_2^- with bisulfite

$$Cl_2^- + HSO_3^- \rightarrow 2Cl^- + SO_3^- + H^+. \qquad (R5)$$

A rate constant at pH 7 has been reported for this reaction (Hasegawa and Neta, 1978), but the value, $3.3 \times 10^7 M^{-1}s^{-1}$, appears low when compared with the rate constants for the other dihalide radicals, Br_2^- and I_2^- (Neta and Huie, 1985a). In this earlier work, the Cl_2^- was produced by reaction of Cl^- with SO_4^-, which in turn was produced by reduction of peroxydisulfate, $S_2O_8^{2-}$

$$e_{aq}^- + S_2O_8^{2-} \rightarrow SO_4^- + SO_4^{2-}. \qquad (R6)$$

It is conceivable that an additional reaction complicates this system (see below) and, therefore, we sought an alternate source of Cl_2^-. Chloride radicals also can be produced using OH radicals, but the mechanism can be complex due to the various equilibria involved

$$OH + Cl^- \leftrightarrow HOCl^- \qquad (R7)$$

$$HOCl^- + H^+ \rightarrow H_2O + Cl \qquad (R8)$$

$$Cl + Cl^- \leftrightarrow Cl_2^-. \qquad (R4)$$

At low pH (3 and below), the dehydration of $HOCl^-$ is rapid and this becomes a viable source of Cl_2^-. Therefore, we have used this system to reinvestigate the reaction of the dichloride radical anion with bisulfite. The Cl^- concentration (and the ionic strength) was 0.1 M, to force reaction (7) to completion rapidly and the pH was 3. The results are presented in Fig. 1. From this plot of the first order rate constant against chloride concentration, a second order rate constant of $3.4 \times 10^8 M^{-1}s^{-1}$ was derived. Including the uncertainty in the determination of bisulfite concentration, we estimate an uncertainty of 10% in this value.

This new value for the rate constant for Cl_2^- $+ HSO_3^-$ is compared with the results for the other

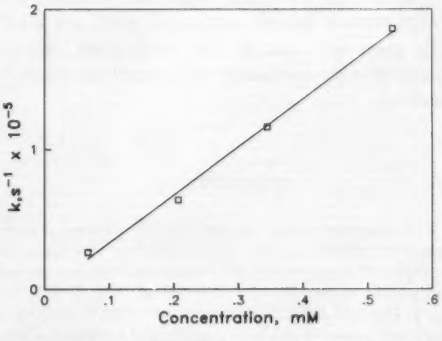

Fig. 1. First-order rate constant for the reaction of Cl_2^- with HSO_3^- as a function of added HSO_3^-.

dihalide radicals Br_2^- and I_2^- in Fig. 2, where the rate constants for the sulfite and bisulfite reactions are plotted against redox potential of the dihalide radical. As predicted from its higher redox potential, the dichloride radical is the most reactive. Although we were not able to measure the rate constant for $Cl_2^- + SO_3^{2-}$, Fig. 2 suggests that its value is not too different from $Cl_2^- + HSO_3^-$.

(3) $SO_4^- + HSO_3^-/SO_3^{2-}$

The difference between the present result and that reported previously for $Cl_2^- + HSO_3^-/SO_3^{2-}$ suggests some unforeseen complication in the pulse radiolysis of a $Cl^-/SO_3^{2-}/S_2O_8^{2-}$ system. A related system, containing sulfite and peroxydisulfate, has been used to derive rate constants for $SO_4^- + SO_3^{2-}$ (Hayon *et al.*, 1972; Chawla, 1973). Rate constants of $> 5.3 \times 10^8$ and 2.6×10^8 $M^{-1}s^{-1}$ were reported. Comparison with the rate constant for the reaction of NO_3 with HSO_3^-/SO_3^{2-} suggests, however, that the rate constant should be greater than 2×10^9 $M^{-1}s^{-1}$ (Neta and Huie, 1986).

We also have carried out a study of the pulse radiolysis of $HSO_3^-/S_2O_8^{2-}$ and $SO_3^{2-}/S_2O_8^{2-}$ solutions. We obtained apparent second-order rate constants of 4.6×10^8 and 8×10^8 $M^{-1}s^{-1}$ for SO_3^{2-} and HSO_3^-, respectively. At low S(IV) concentrations, however, the first-order fits were not particularly good, and the high concentration datum for HSO_3^- was much lower than that predicted from the lower concentration points. We suggest that a chain reaction which regenerates SO_4^- takes place in this system. We speculate that it involves the reduction of the peroxydisulfate by the sulfite radical, either by electron or O^- transfer

$$S_2O_8^{2-} + SO_3^- \rightarrow SO_4^{2-} + S_2O_7^- \quad \text{(R9)}$$

$$S_2O_7^- \rightarrow SO_4^- + SO_3 \quad \text{(R10)}$$

or

$$S_2O_8^{2-} + SO_3^- \rightarrow S_2O_8^{3-} + SO_3 \quad \text{(R11)}$$

$$S_2O_8^{3-} \rightarrow SO_4^- + SO_4^{2-}. \quad \text{(R12)}$$

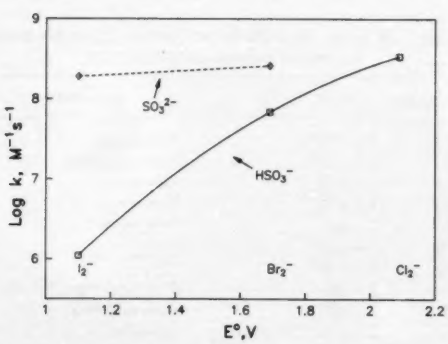

Fig. 2. Second-order rate constants for the reactions of dihalide radicals with S(IV) species as a function of the dihalide redox potential. A smooth curve has been drawn through the HSO_3^- data.

This would slow the rate of loss of SO_4^-, leading to too low a rate constant for the primary reaction. A similar chain would then be expected in the Cl_2^- case, explaining the anomalously low rate constants obtained there.

(4) $SO_5^- + HSO_3^-/SO_3^{2-}$

A key chain propagating reaction in the autoxidation of aqueous SO_2 is the reaction of the peroxysulfate radical with sulfite and bisulfite. There are two likely paths for this reaction: one leading to sulfate (or bisulfate) and the sulfate radical by oxygen atom transfer;

$$SO_5^- + SO_3^{2-} \rightarrow SO_4^- + SO_4^{2-} \quad \text{(R13a)}$$

the other leading to peroxymonosulfate and the sulfite radical by electron transfer

$$SO_5^- + SO_3^{2-} + H^+ \rightarrow HSO_5^- + SO_3^-. \quad \text{(R13b)}$$

Unfortunately, there is no substantial information on the branching ratio between these two paths (Neta and Huie, 1985b). Since compounds such as alcohols, which can react with SO_4^- but not SO_3^- (Neta and Huie, 1985b), inhibit sulfite autoxidation, the first path is likely to be important. But since peroxymonosulfate is produced in the autoxidation reaction (Deuvyst *et al.*, 1979) in up to a 30% yield, the second path also is likely to take place. In our subsequent discussion, we assume the paths proceed in a 3:1 ratio.

In our earlier work (Huie and Neta, 1984), we derived a rate constant for reaction (13) at pH 6.8 by measuring the effect of added sulfite on the rate of formation of the ascorbate radical after the pulse radiolysis of a 5 mM ascorbate solution saturated with a 1:1 mixture of $N_2O:O_2$. In the present work, we have carried out similar experiments at pH 8.7 and 4.9 to determine the rate constants for the reactions of SO_3^{2-} and HSO_3^-, respectively.

The results were analyzed using the mechanism below (Huie and Neta, 1984) (rate constant units, $M^{-1}s^{-1}$):

$$SO_3^- + O_2 \rightarrow SO_5^- \qquad k = 1.5 \times 10^9 \quad \text{(R14)}$$

$$SO_3^- + Asc \rightarrow SO_3^{2-} + Asc\cdot \qquad k = 9.0 \times 10^6 \quad \text{(R15)}$$

$$SO_5^- + Asc \rightarrow HSO_5^- + Asc\cdot \qquad k = 1.4 \times 10^8 \quad \text{(R16)}$$

$$SO_5^- + SO_5^- \rightarrow S_2O_8^{2-} + O_2 \qquad k = 1.4 \times 10^8 \quad \text{(R17a)}$$

$$\rightarrow 2SO_4^- + O_2 \qquad k = 6.0 \times 10^8 \quad \text{(R17b)}$$

$$SO_4^- + SO_3^{2-} \rightarrow SO_4^{2-} + SO_3^- \qquad k = 2 \times 10^9 \quad \text{(R18)}$$

$$SO_4^- + Asc \rightarrow SO_4^{2-} + Asc\cdot \qquad k = 1 \times 10^9 \quad \text{(R19)}$$

$$SO_3^- + SO_3^- \rightarrow S_2O_6^{2-} \qquad k = 7.0 \times 10^8 \quad \text{(R20)}$$

$$SO_5^- + SO_3^{2-} \rightarrow HSO_5^- + SO_3^- \quad \text{(R13a)}$$

$$\rightarrow SO_4^{2-} + SO_4^-. \quad \text{(R13b)}$$

First-order rate constants for the formation of the ascorbate radical were calculated at a fixed ascorbate concentration and at several concentrations of sulfite. Then predicted first-order rate constants were determined by computer modeling the above mechanism, using several values for the rate constant of reaction (13). The results are given in Table 1 for $k(13) = 1.3 \times 10^7\ M^{-1}s^{-1}$. The agreement is very good, and the results did not appear to depend too strongly on the branching ratio for reaction (17). Although the extent of this agreement is encouraging, the uncertainty in the mechanisms for reactions (13) and (17) limits the accuracy of this value. We estimate, however, that it is good to within 50%.

Similar experiments were carried out at pH 4.9. The effect of adding bisulfite on the measured rate of ascorbate radical build-up, however, was not very large. Still, we were able to deduce a value of $3 \times 10^5\ M^{-1}s^{-1}$ for the reaction of SO_5^- with HSO_3^-. This calculation assumed that there is no SO_3^{2-} present at this pH. At the ionic strength of the solution (0.5 M), however, this assumption probably is not valid. Indeed, recalculating the equilibrium concentrations using the ionic strength correction factors suggested by Clarke (1981), we find that the concentration of SO_3^{2-} is sufficient to explain the observed effect of added bisulfite. This would suggest that the rate constant for the reaction of SO_5^- with HSO_3^- is less than $3 \times 10^5\ M^{-1}s^{-1}$.

Similar experiments using ascorbic acid could not be carried out at lower pH due to the pK of ascorbic acid, so an attempt was made to use hydroquinone as the reference reactant at pH 3.4. Unfortunately, we found that the rate constant for the disproportionation of the product semiquinone at this pH and ionic strength ($k \sim 1 \times 10^9$), coupled with the rate of reaction of the semiquinone with O_2 ($k \sim 1 \times 10^7$), resulted in a significant loss of the semiquinone product. This complicated the modeling calculations seriously. It was apparent that the reaction of SO_5^- with HSO_3^- is slow ($< 10^6\ M^{-1}s^{-1}$), however, but a reliable estimate of its value could not be derived.

DISCUSSION

In this work, we have redetermined the rate constants for three of the most critical reactions in the radical-induced oxidation of SO_2 in atmospheric droplets. For the reaction of the OH radical with bisulfite, we have measured a rate constant a factor of 2 lower than that reported previously. For the reaction of the dichloride radical with bisulfite, the rate constant is a factor of 10 higher. For the reaction of the peroxysulfate radical with bisulfite, only a upper limit could be determined, but this upper limit is a factor of 10 lower than that used in the models. In addition, our results here and in previous work (Neta and Huie, 1986), suggest that the reaction of the sulfate radical with bisulfite is also faster than previous experiments suggested.

Table 1. Rate of formation of the ascorbate radical as a function of added sulfite*

Sulfite	k(observed) (s^{-1})	k(model) (s^{-1})
19.3 mM	2.01×10^5	2.12×10^5
49.7 mM	1.62×10^5	1.59×10^5
99.55 mM	1.21×10^5	1.17×10^5
146 mM	0.96×10^5	0.97×10^5

* 2.05 mM Ascorbic acid; 0.49 M $NaClO_4$; N_2O; O_2 = 1:1; pH 8.7.

We have investigated roughly the impact of these new rate constants on the free radical induced oxidation of SO_2 in atmospheric droplets. A very simple approach was taken, assuming a homogeneous source of OH radicals ($1 \times 10^{-9}\ M\ s^{-1}$), and constant S(IV) and O_2 concentrations (4.9×10^{-6} M and 2.6×10^{-4} M). We start by assuming the basic chain mechanism:

Initiation:

$$OH + HSO_3^{2-} \rightarrow H_2O + SO_3^- \qquad (R21)$$

$$SO_3^- + O_2 \rightarrow SO_5^- \qquad (R14)$$

Propagation:

$$SO_5^- + HSO_3^- \rightarrow HSO_5^- + SO_3^- \qquad (R13a)$$

$$\rightarrow HSO_4^- + SO_4^- \qquad (R13b)$$

$$SO_4^- + HSO_3^- \rightarrow HSO_4^- + SO_3^- \qquad (R18)$$

$$SO_5^- + SO_5^- \rightarrow 2SO_4^- + O_2 \qquad (R17b)$$

Termination:

$$SO_5^- + SO_5^- \rightarrow S_2O_8^{2-} + O_2 \qquad (R17a)$$

$$SO_3^- + SO_3^- \rightarrow S_2O_6^{2-}. \qquad (R20)$$

With this mechanism, and the rate constants given in Table 2, we calculate a sulfate concentration of 5.7×10^{-6} M at 1000 s. If the rate constant for $SO_5^- + SO_3^{2-}$ (1.4×10^7) is used for reaction (13), a sulfate concentration of 2.0×10^{-4} M is calculated at 1000 s.

Table 2. Rate constants for the reactions in the simple model for radical-induced SO_2 oxidation

Reaction	$k(M^{-1}s^{-1})$	Reference
21	4.5×10^9	This work
14	1.5×10^9	Huie and Neta (1984)
13a	2.5×10^4	This work
13b	7.5×10^4	This work
18	2×10^9	This work
17a	1.4×10^8	
17b	6.0×10^8	
20	1×10^9	Ross and Neta (1979)
22	2×10^8	Ross and Neta (1979)
4	2.1×10^{10} (forward) 1.1×10^5 (reverse)	Jayson *et al.* (1973)
5	3.4×10^8	This work
23	3.4×10^9	Estimate
24	1.0×10^9	Navaratnam *et al.* (1980)

The effect of added chloride can be investigated by adding the additional reactions:

$$SO_4^- + Cl^- \rightarrow SO_4^{2-} + Cl \quad (R22)$$

$$Cl + Cl^- \leftrightarrow Cl_2^- \quad (R4)$$

$$Cl_2^- + HSO_3^- \rightarrow 2Cl^- + H^+ + SO_3^- \quad (R5)$$

$$Cl + HSO_3^- \rightarrow Cl^- + H^+ + SO_3^- \quad (R23)$$

$$Cl_2^- + HO_2 \rightarrow O_2 + H^+ + 2Cl. \quad (R24)$$

A chloride concentration of 5×10^{-4} M was assumed. When the higher rate constant for (R13) was used, a sulfate concentration of 1.63×10^{-4} M after 1000 s was calculated; when the lower value was used, a concentration of 5.53×10^{-6} M was calculated. With this mechanism, then, the effect of added chloride does not appear to be particularly great.

A major difference between the mechanism above and that used by McElroy (1986) is that the self-reaction of SO_5^- is not assumed to be primarily a termination reaction (R17a), but is assumed to be mostly a chain propagating reaction (R17b), in accord with the results of Thompson (1981). We have investigated the consequences of this assumption by reversing the rate constants chosen for reaction (17). After 1000 s, with the low value for (R13), we get a sulfate concentration of 9.0×10^{-7} M, showing that the calculated production of sulfate is quite sensitive to the mechanism chosen for (R17).

Due to the slowness of the reaction of SO_5^- with HSO_3^-, other reactions of the peroxysulfate radical become very important, particularly the self-reaction. SO_5^- also could react with reductants in the droplet, including O_2^- and reduced metal ions, or could undergo cross-disproportionation reactions with organic peroxy radicals, which also appear to be unreactive toward bisulfite (Huie and Neta, 1986). It is obvious that the mechanisms of these secondary radical–radical reactions are of considerable importance for a complete understanding of the radical induced oxidation of SO_2 in atmospheric droplets.

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